Solving Nonlinear Eigenvalue Problems in Electronic Structure Calculations

Chao Yang* and Juan Meza *

The Kohn-Sham (KS) equations arise in electronic structure calculations, which are nowadays an essential tool for studying the quantum mechanical properties of molecules, solids and other nanoscale materials. Through the density functional theory formalism, one can reduce the many-body Schrodinger equation, which is a linear eigenvalue problem, to a set of single-electron KS equations that have far fewer degrees of freedom. However, the price one has to pay is to solve a nonlinear eigenvalue problem in which the Hamiltonian is a function of the desired but unknown eigenfunctions to be computed. Currently, the most widely used numerical algorithm for solving this type of problem is the Self-consistent field (SCF) iteration. This algorithm can be viewed as a fixed point iteration in which approximations to the eigenvectors of a fixed Hamiltonian are computed at each iteration, and these eigenvectors are used to update the Hamiltonian for the next iteration. However, it is well known that the simplest form the SCF iteration often fails to converge to the correct solution. We will analyze the convergence properties of the SCF iteration and discuss several strategies for preventing it from diverging. Because the KS equations represent the first order necessary conditions of a constrained minimization problem in which the total energy of an atomistic system is minimized subject to orthonormality of the electron orbitals, an alternative approach is to apply a constrained minimization algorithm to solve the energy optimization problem directly. We will describe a recently developed iterative constrained minimization algorithm in which the total energy is minimized in a sequence of overlapping subspaces. The minimizer of each subspace energy functional not only provides a search direction along which the total energy functional decreases but also gives an optimal "step-length" to move along this search direction. Numerical examples will be presented to demonstrate the efficiency and accuracy of this approach and compare it with the SCF iteration.

*Computational Research Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720.